AN INVESTIGATION OF THE VAPOR-LIQUID EQUILIBRIUM AT PRESSURES BELOW ONE ATMOSPHERE FOR THE SYSTEM: METHYL BENZOATE - ISOPROPYL BENZOATE

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crosland

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Approved:

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I wish to express my sincerest thanks to Doctor W. M. Newton for suggesting this most interesting problem and for his invaluable suggestions in the course of its prosecution. I also wish to express appreciation to my wife, Wilma Jean, for her fine cooperation in helping compile and type the thesis.

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NOMENCLATURE

x_1	mole fraction of methyl benzoate in liquid
y_1	mole fraction of methyl benzoate in vapor
x_2	mole fraction of isopropyl benzoate in liquid
y_2	mole fraction of isopropyl benzoate in vapor
p_1	partial pressure of methyl benzoate in vapor
p_2	partial pressure of isopropyl benzoate in vapor
P_T	Total vapor pressure
P_1°	vapor pressure of pure methyl benzoate
P_2°	vapor pressure of pure isopropyl benzoate

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INTRODUCTION

Vapor liquid equilibrium data are available for comparatively few of the common binary solutions[1,2,3] and for almost no ternary solutions.

This study is a part of a more extensive investigation of the effect of reduced pressures on the efficiency of a laboratory distillation column packed with glass helices. For this investigation it was decided to use a binary mixture composed of methyl benzoate and isopropyl benzoate. Inasmuch as vapor liquid equilibrium data for this system of benzoates are not available in the literature, column efficiency could not be determined unless possibly Raoult's Law for ideal solutions could be assumed. However the validity of this assumption was not

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1. Fowler, W. T., "The Evolution of the Equilibrium Still," The Industrial Chemist, 24, 828 (Dec. 1948).

2. Struck, Robert T. and Kinney, Corliss R., "Effeciency of Packed Fractionating Columns," Industrial and Engineering Chemistry, 42, 77 (Jan. 1950).

3. Gilmont, Roger; Othmer, Donald F., et. al.; "Thermodynamic Correlation of Vapor Liquid Equilibria," Industrial and Engineering Chemistry, 42, 120 (Jan. 1950).

known for sure and, consequently, the experimental study of the vapor liquid equilibrium was undertaken.

There have been many types of equilibrium stills used by various experimenters[4] but the one chosen for this work was a new "Othmer" type equilibrium still[5] made by The Emil Greiner Company. It was chosen because it represents the most recent developments and because many of the defects of previous equilibrium stills have been eliminated. Using this still in conjunction with auxiliary equipment to maintain the proper pressures and temperatures in the system, the vapor-liquid equilibrium concentrations were determined at seven pressures between 5 mm. Mercury and 760 mm. Mercury absolute pressure.

The resultant equilibrium curves of mole percent Methyl Benzoate in the liquid phase versus mole percent Methyl Benzoate in the equilibrium vapor phase are shown in Figure 12. The accuracy of the curves is of the order of one percent.

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4. Fowler; op. cit., p. 717 ff.

5. Othmer, Donald F.; "Composition of Vapors from Boiling Solutions," Analytical Chemistry, 20, 763-766 (Aug. 1948).

CHOICE OF BINARY MIXTURE

Methyl benzoate and isopropyl benzoate were chosen to work with in investigating column efficiency at reduced pressures because they appeared to possess many of the preferred characteristics of a binary mixture or its components, for determining the efficiencies of packed columns.

The preferred characteristics of any binary mixture, or its components, used for determining the efficiencies of columns were listed by M. R. Fenske, et. al.[6].

> "The components should be obtainable in a high state of purity.
> The components should be relatively inexpensive if columns of large capacity are to be tested.
> The components should be of the same type as those regularly used in the columns.
> The mixture should be stable and non corrosive in the columns.
> The mixture should allow condensation without resorting to refrigerative cooling.
> The mixture should be capable of easy and accurate analysis.
> The mixture should be as nearly ideal as possible, the components being completely miscible at all the temperatures used, no azeotropes being formed, and the relative volatility being substantially constant, for a given pressure, over the entire concentration range.
> The vapor liquid equilibrium diagram should be available at the pressure used in testing, if a perfect solution is not formed and if the relative volatilities existing over the concentration range to be worked in are not known.

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6. Fenske, M. R.; Myers, H. S.; and Quiggle, Dorothy; "N-Decane-trans-Decahydro-Naphtalene," Industrial and Engineering Chemistry, 42, 649 (April 1950).

The boiling points of the two liquids should be close enough so that, under the conditions of test, neither component is produced in a high state of purity. When this is the case, it is usually easier to obtain a more accurate analysis of the still and condenser samples. At the same time, the boiling points of the two liquids should not be so close that differences in pressure between the top and bottom of the fractionating section result in a considerably different number of plates calculated, depending on whether the relative volatility existing at the top or the bottom of the section or some average value is used in making the calculations. This factor is especially important when operating at reduced pressures, where the pressure drop through the fractionating section may be appreciable in comparison with the pressure at the top of the section.

Another desirable property is that the relative volatility should decrease with decreasing pressure.[7]

This investigation shows that the benzoates chosen do not entirely follow all of the preferred characteristics over the entire pressure range. The isopropyl benzoate appears to decompose slightly upon continuous boiling at pressures above 200 mm. mercury absolute pressure since a yellowish color appears in the still liquid. The color is apparently given by a solid material because distillation to dryness did not distill over any colored material. The isopropyl benzoate showed a decreased refractometer scale reading of 0.08 units after setting two months but upon boiling for two hours at 760 mm mercury the reading regained its previous value and then rose 0.08 units. An increase

7. Struck and Kinney; op. cit., p. 77.

in scale reading causes a greater apparent concentration of methyl benzoate.

Physical data available on the benzoates are given in Tables I, II, III, IV, and V. From these it may be seen that most of the preferred characteristics are present.

The benzoates are water clear liquids possessing a sweetish odor which is rather overpowering in concentrated form. They are used to some extent as perfumes in such articles as hair tonic and soap and as a high boiling solvent for inks. They dissolve rubber readily, dissolve silicone stopcock grease, remove paint or baked enamel, and have even partially dissolved the cement around the prisms of the refractometer.

HISTORY OF EQUILIBRIUM STILLS

The history of equilibrium stills goes back to the 19th century[8]. The first stills were merely large boilers with a condenser for making batch distillations. By using a large enough sample and extrapolating successive samples back to the starting time the initial equilibrium concentrations could be guessed at with fair accuracy. The process was long and time consuming as well as inaccurate and soon gave way to modifications of various natures.

A rather good account of the history of equilibrium stills has been presented in a paper by R. T. Fowler[9]. He presents a diagram and brief discussion of some thirty of the foremost developments during the past 80 years and gives his analysis of their faults and virtues. His comment on the older type Othmer still was that "it is easily constructed and reasonably good results are obtained[10]."

Since the excellent review of equilibrium stills by Fowler is readily available, it would be rather purposeless to repeat the detailed information here and the reader is therefore referred to the article.

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8. Fowler; op. cit., p. 717.

9. ibid., p. 717 ff.

10. ibid., p. 829.

EQUIPMENT AND ACCESSORIES

The new "Othmer" type still[11] is shown diagramatically in Fugures 1 and 2 and was made by The Emil Greiner Company. It is essentially an 800 ml. Kjeldahl flask with glass tubing connections for leaving vapor and returning condensate. It differs from the earlier Othmer stills in several ways. The neck of the flask has been shortened to minimize refluxing, the condenser has been changed from parallel flow of vapor and condensed liquid to countercurrent flow to minimize absorption of inert gases with subsequent release in the flask where they could cause superheating by collecting around the vapor outlet tube, and a rim has been added at the neck of the flask to guide any vapor which does condense prematurely into the condensate receiver rather than into the flask as reflux.

Heating is provided by a 250 watt nichrome wire heating coil wound on one leg of a U shaped tube attached to the base of the flask. The wound leg is centrally located and approximately 6 inches in length and 1 inch in diameter. The natural circulation of the liquids caused

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11. Othmer, Donald F.; "Composition of Vapors from Boiling Solutions," Analytical Chemistry, 20, 763, (Aug. 1948).

LEGEND FOR FIGURES 1 AND 2

a 6X 1 inch boiling leg wound with a 250 watt nichrome wire heating coil

b downtake side of boiling leg

c liquid sample stopcock

d vapor sample stopcock

e 30 ml. vapor sample tube, or condensate receiver, with 24/40 \$ ground glass joint.

f condensate tube to provide positive displacement of liquid in condensate receiver

g drop counter

h 800 ml. Kjeldahl flask without long neck

i central vapor outlet tube 1 X 3 inches

j opening for adding liquids or venting gases

k protective rim to prevent reflux

l one inch vapor outlet tube

m 24/40 \$ ground glass joint for thermocouple well

n 29/42 \$ ground glass joint for 12 inch ball type condenser with 1 inch outlet line

o four inch condenser for super cooling condensate

p return line to still for condensate

q leads to variac

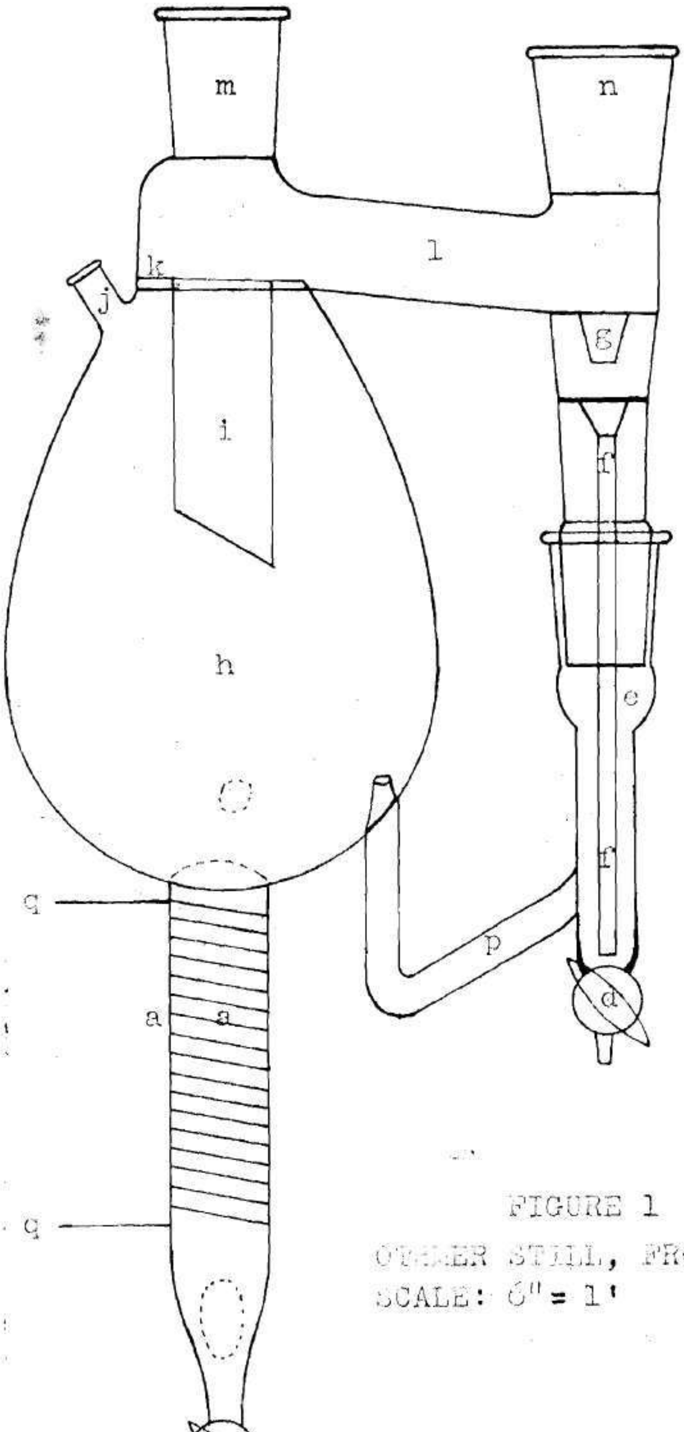

FIGURE 1
OTHMER STILL, FRONT VIEW
SCALE: 6" = 1'

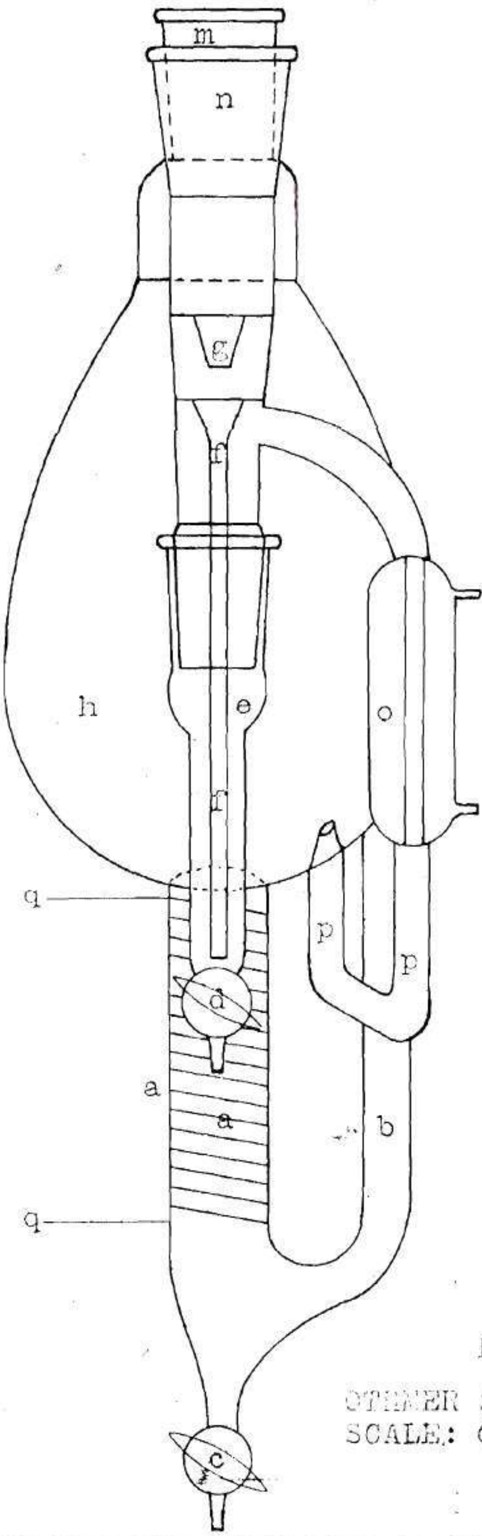

FIGURE 2

OTHMER STILL, SIDE VIEW
SCALE: 6" = 1'

by this design provides adequate mixing action to prevent returning condensate from flashing.

The condensate being composed of a higher percentage of the lower boiling component will have a lower boiling point. Therefore, unless mixing occurs quickly, the condensate will be superheated and flash into vapor again since the liquid in the still is above the boiling point of the condensate.

The vapors rising from the liquid surface rise over a thermocouple well centrally located in the 1 inch vapor outlet tube which projects approximately 3 inches down into the flask. The tip of the thermocouple is at the lower end of the vapor outlet tube and $1\frac{1}{2}$ inches above the liquid. The vapors then pass to the main condenser, drip down through the drop counter, and return to the still through a small 4 inch condenser which further cools the condensate to help prevent flashing. When the condensate drips through the drop counter it enters a long tube extending to the base of the 30 ml. capacity vapor sample tube such that positive displacement of the condensate is assured.

Samples may be taken at equilibrium through stopcocks located at the bottom of the boiling leg for the liquid sample and at the bottom of the vapor sample tube for the vapor sample.

The still was enclosed in an air bath comprised of a 3/8 inch plywood box 11 inches square and lined with 3/8 inch of asbestos. A floor was installed just above the liquid sample stopcock while the ceiling was about 3 inches above the top of the flask. Heating of the air bath was provided by coils of number 20 nichrome wire draped along the inner sides of the box approximately on a level with the liquid level in the flask and from 1 to 4 inches away from the still surface. The total resistance was such that the coils reached red heat at 130 volts as controlled by a variac transformer. To prevent localized heating a 4 inch fan blade was used to keep the air circulating inside the box. The fan shaft projected through the left side of the box to an Eastern Industries variable speed stirring motor.

Observation of the still was possible through a 3 inch square double pane window installed in the front of the box and facilitated by means of a 15 watt light bulb mounted on the left wall of the box. The end of the bulb was within $1\frac{1}{2}$ inches of the side of the still.

The temperature of the vapors from the boiling liquids was measured with an iron-constantan thermocouple by means of a Leeds and Northrop potentiometer. A reference junction for the potentiometer of 0° C. was provided through dual use of the system's cold trap.

The pressure in the system was measured with an absolute manometer constructed of $\frac{1}{4}$ inch glass tubing. The difference in the heights of the mercury columns was measured with an ordinary meter stick which fitted very closely to the glass tubing; so that a reading accurate to $\frac{1}{4}$ mm. mercury pressure was obtainable. The manometer was evacuated of air and water by carefully boiling bubbles of mercury the entire length of the manometer from the closed end to the open end. It was then tested for accuracy with a General Electric McLeod gauge at $\frac{1}{2}$, 1, and 2 mm. of mercury.

Pressure regulation was provided by a cartesian diver type of manostat[12] built by The Emil Greiner Company (Figure 3.). At pressures from 5 to 200 mm. of mercury the regulation was good i.e., the manometer reading was constant, but at higher pressures the pressure difference across the orifice in the regulator was so great that a gradual leakage occurred causing the pressure in the system to drop slowly. However, since the system was almost air tight and a 10 liter reservoir to absorb pressure fluctuations was included in the system, the higher pressures could be maintained merely be adjusting the pressure exactly once boiling had started and closing all stopcocks. About once an hour a 1 mm. rise

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12. Gilmont, Roger; "Theory and Operation of a Cartesian Diver Type of Manostat," Industrial Engineering Chemistry, Analytical Ed., 18, 633 (1946).

LEGEND FOR FIGURE 3: MANOSTAT

a float or "cartesian diver"

b rubber filled head of float

c tube connecting inside of float to system through stopcock f

d connection to still side of system

e connection to pump side of system

f three way stopcock

g tube connecting orifice to vacuum side of system

h orifice tipped tube through which excess gas is evacuated

i mercury

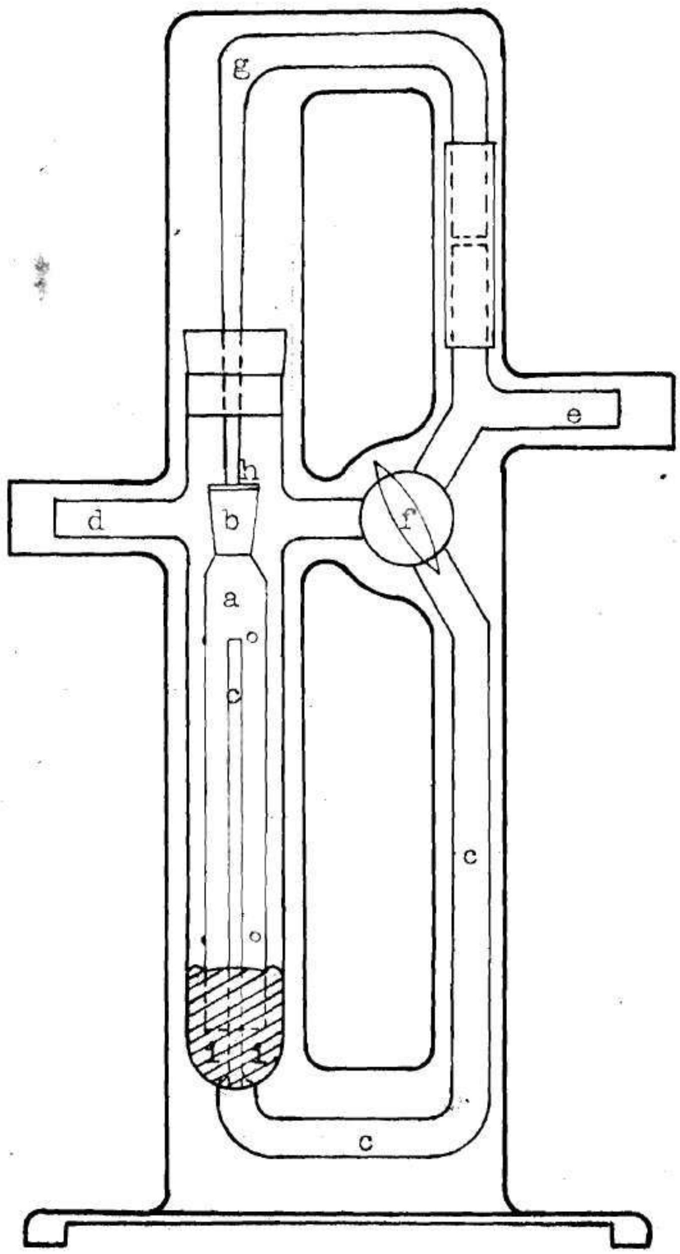

FIGURE 3: MANOSTAT (PRESSURE REGULATOR)

in pressure had to be reduced. The vacuum was provided by a Cenco Pressovac pump operated by a 1/3 horsepower Emerson electric motor.

Referring to Figure 3, the operation of the manostat and the procedure used will be briefly described. The system was adjusted to the desired pressure with stopcock f open so that the same pressure existed on both sides of the orifice h and inside of the float a (cartesian diver). The diver floats on mercury. When the desired pressure was attained stopcock f was closed and the pump side of the system, e, evacuated. The pressure trapped in the float then controlled the pressure in the still side of the system. If the pressure was correct or too low the top of the float, which is filled with soft rubber b, sealed off orifice h such that no gas was removed from the still. However, if the pressure rose in the still through leakage, the float dropped $\frac{1}{4}$ inch and allowed the excess gas to be pumped out through orifice h. The above operation controlled the pressure exactly so long as the pressure in the float remained constant and the pressure difference across the orifice was not too great. If, however, the temperature of the room should increase appreciably after the first adjustment, the pressure in the float would also increase because of thermal expansion and give a higher controlling pressure, and visa versa for a decrease in the room temperature. Readjustment would then be necessary in either case. The pressure regulator is said to be turned on when stopcock f is closed.

The equilibrium samples were analyzed with a Bausch and Lomb modified Abbe type precision reffactometer[13]. The prism hinge is vertical instead of horizontal, a monochromatic sodium D light is provided (no compensator system necessary), and the refractometer scale is horizontal and of the equidivision type with an accompanying calibration chart of scale reading versus refractive index. Because the scale is equidivision more accuracy per scale division is provided at the upper end of the scale where the change in refractive index per scale division is only 1/3 the change at the lower end of the scale. The entire range of refractive indices is covered by two of these instruments. At 25° C. the two liquids used in this work had refractive indices on the lower end of the scale of the higher range instrument. Since refractive index decreased with increase in temperature the temperature for analysis was raised to 43° C. to enable the upper end of

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13. Weissberger, Arnold; *Technique of Organic Chemistry, Vol. I, Part II Physical Methods of Organic Chemistry*, Interscience Publishers Inc., New York, pp. 1209-1213 (1949).

the scale of the lower range instrument to be used. The increase in accuracy provided another significant figure in the analysis of samples.

EXPERIMENTAL LIQUIDS

The reagent glacial acetic acid conforming to A.C.S. specifications and suitable for microanalysis was manufactured by Merck and Company and was rated as 99.5 percent $HC_2H_3O_2$. It was not distilled before use.

The distilled water was furnished by a Barnstead Laboratory water still.

The methyl benzoate was made by the Matheson Company and advertised to be of highest purity. This liquid was distilled in a packed distillation column constructed by Leonard R. Daniel for his present work on efficiencies at reduced pressures.* The packed section, 30 inches high by 2 inches in diameter, was packed with 8 turn glass helices 1/8 inch in diameter and $\frac{1}{2}$ inch long. The still was operated at a 10 to 1 reflux ratio at 20 mm. of mercury absolute pressure. The distillate was tested every 10 ml. until a constant reading of refractive index was established. This occurred after the second sample although the first five samples were discarded. Distillation was discontinued when the boiling temperature started to rise. The still bottoms contained large quantities of benzoic acid and were discarded.

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* Daniel, Leonard R.; Georgia Institute of Technology.

Then, after the distillate was redistilled using the same procedure, the still was washed with soapy water, tap water, and distilled water and thoroughly dried.

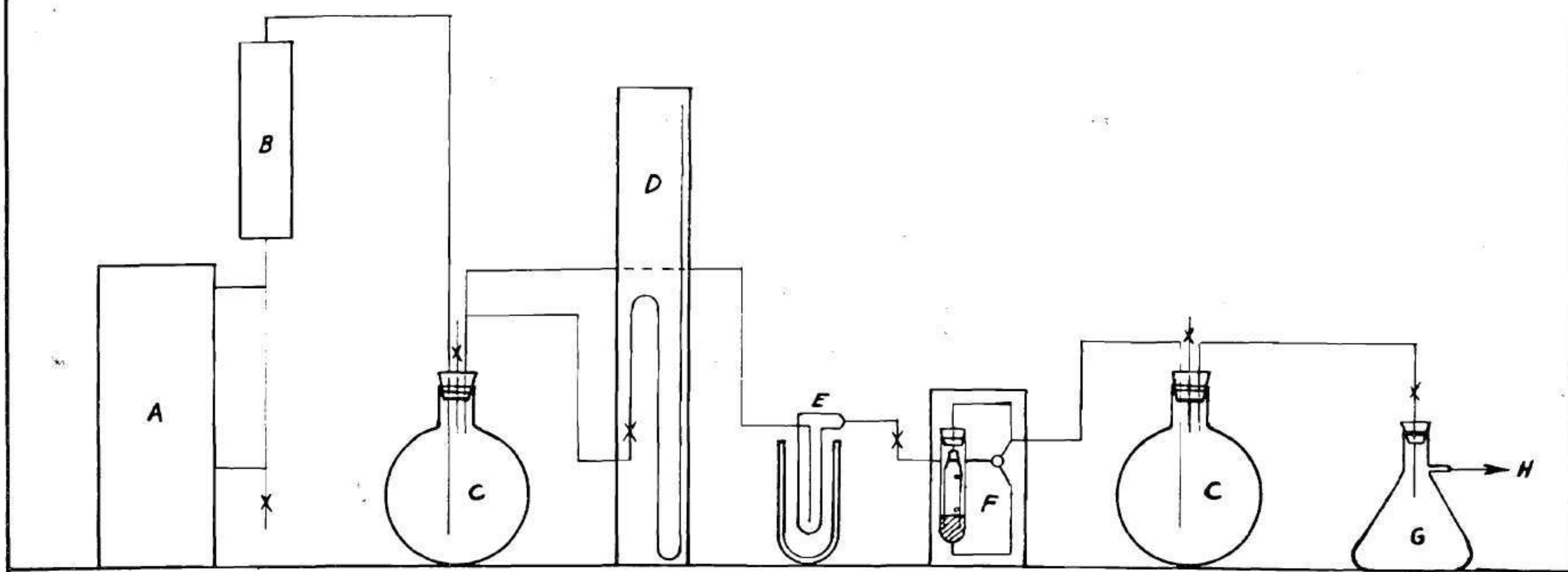
The isopropyl benzoate was made partly by The Eastman Kodak Company and partly by The Matheson Company. The two varieties were mixed and distilled in the same column used for the methyl benzoate and following the same procedure.

EXPERIMENTAL PROCEDURE AND RESULTS

OPERATION OF STILL

The equipment was set up as shown diagramatically in Figure 4. The still was filled with approximately 350 cc. of pure component or mixture, the system was closed, and the pressure adjusted to the desired value. The pressure regulator was turned on and heat was gradually applied to the still and to the air bath by means of variac transformers supplied with 110 volt constant voltage. When slow boiling occurred the heat input to the air bath was adjusted so that condensation just occurred on the upper part of the still. The condensation was not fractionation but was just enough to indicate that superheating of the vapor was not occurring.

After two hours of boiling at constant pressure, samples were removed and analyzed. This was done by closing the stopcock between the vapor trap and the manostat and letting atmospheric pressure into the still so that the liquid could be withdrawn. The still pressure was then reset by first opening stopcock f of the manostat and then the stopcock between the vapor trap and the manostat. If the manostat stopcock was not opened first the excessive pressure difference would force the mercury up into the float and perhaps cause breakage. The liquid was allowed



A OTHMER STILL
B CONDENSER
C 5-LITER FLASK
D MANOMETER
E COLD TRAP
F MANOSTAT
G 1-LITER FLASK
H TO VACUUM PUMP

FIGURE 4: SCHEMATIC DIAGRAM OF EQUIPMENT

to boil again for an hour and new samples taken. After a succession of samples had established that the still was at equilibrium, the operation was shifted to the next higher pressure range to be investigated.

TEST WITH ACETIC ACID-WATER SYSTEM

When a new piece of equipment is used its reliability must be established. The best way to test an equilibrium still is to make test runs with liquids for which equilibrium data are known.

A large amount of vapor liquid equilibrium data are available for the system ethyl alcohol and water. However, since absolute ethyl alcohol was not readily available and since both glacial acetic acid and some equilibrium data for acetic acid and water were available, the latter system was used for making test runs.

Roger Gilmont and Donald F. Othmer have published[14] some curves and data (Table VI) for the acetic acid-water system at reduced pressures using the older type Othmer still[15] and their results were used for comparison.

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14. Gilmont, Roger and Othmer, Donald F.; "Composition of Vapors from Boiling Binary Solutions," Industrial and Engineering Chemistry, 36, 1061 (Nov. 1944).

15. Othmer, Donald F.; "Composition of Vapors from Boiling Binary Solutions," Industrial and Engineering Chemistry, 35, 614 (May 1943).

In order to analyze the equilibrium samples a standard set of samples of known compositions of acetic acid and water (Table VII) was prepared from which a calibration curve, of refractometer scale reading versus weight percent water was constructed (Figure 5).

The samples used in testing varied from 45 to 65 weight percent water and the procedure of operation of the still was the same as that previously described. The experimental equilibrium values obtained (Table VIII) were compared with the published data of Othmer and Gilmont. In all cases the separation was approximately 2 percent greater than that attained by Othmer and Gilmont (Figure 6).

Various changes were made in rate of boiling and air bath temperature to check the operational procedure. The raschig rings originally packed in the boiling leg of the still in a futile effort to minimize bumping at low pressures were removed. All of these changes made no appreciable difference and the method of analysis was suspected since the samples were analyzed with the refractometer at 43°C. To check the refractometer analysis, a standard base of carbonate free sodium hydroxide was prepared using certified potassium dichromate as a standard acid. Subsequent titration of equilibrium samples with the base, using phenolphthalein indicator, gave substantially the same results as the refractometer analysis.

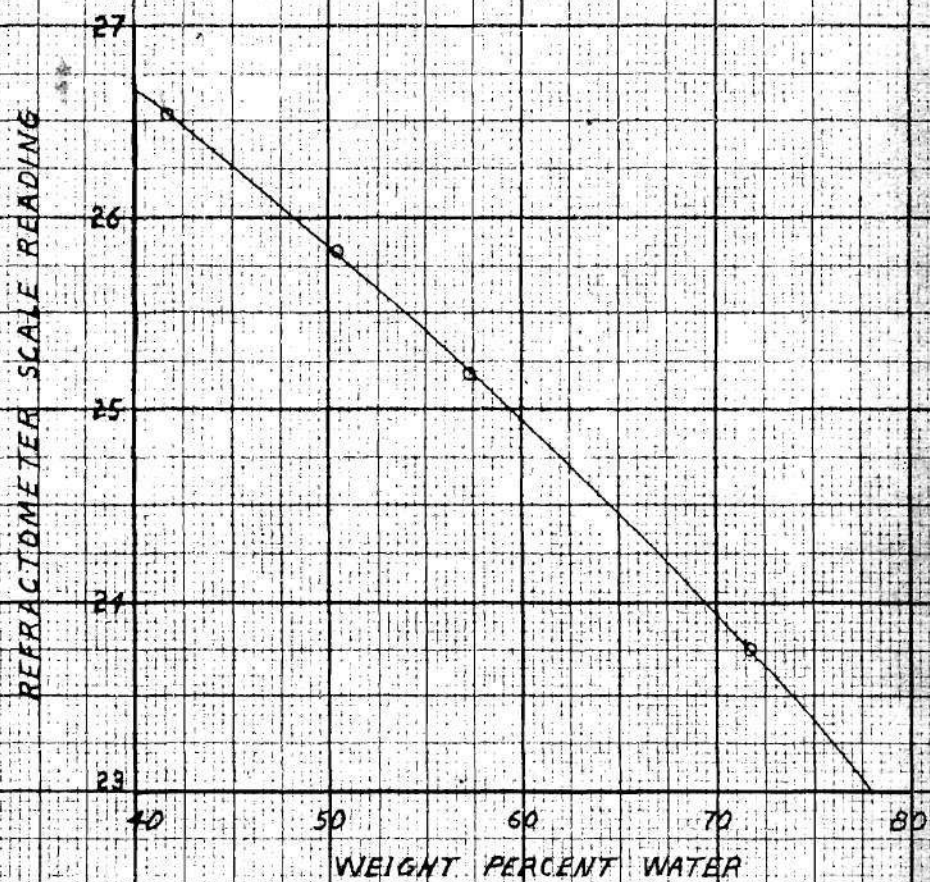

FIGURE 5
REFRACTOMETER CALIBRATION FOR
ACETIC ACID - WATER MIXTURES

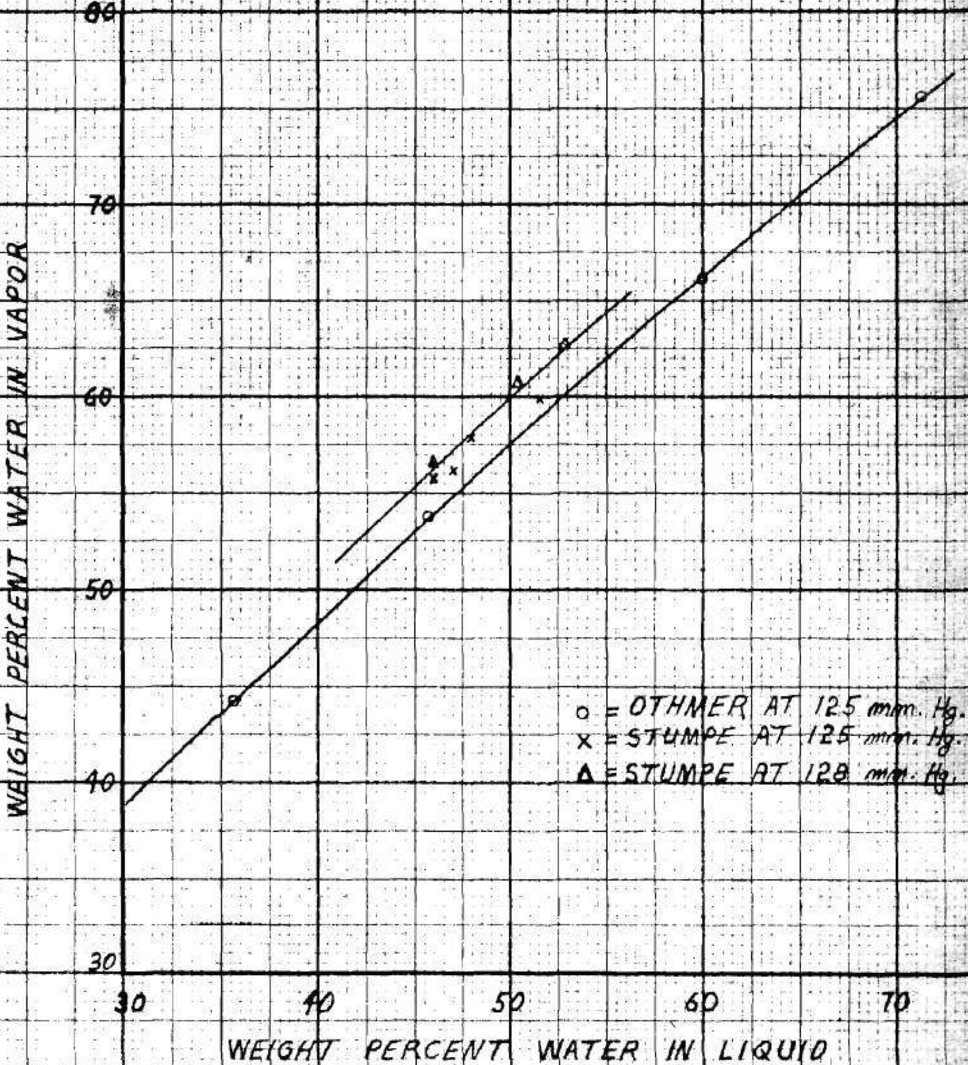

FIGURE 6

EQUILIBRIUM CURVES FOR ACETIC ACID - WATER SYSTEM

Since Othmer and Gilmont used the older type still containing several objectionable features not incorporated in the new type still used in this investigation, it is probably the equipment which has caused the difference in results; and, since the equipment used in this investigation is of improved design, it is believed that these data are more precise.

The variance from the data of Othmer and Gilmont was on the order of magnitude of 2 percent. However, Othmer and Gilmont also published the data of several other experimenters[16] whose results varied up to 5 percent. In general different experimenters with different stills do not seem to agree very well[17].

Struck and Kinney[18] noted in testing a similar still with ethyl alcohol-water that, although their results agreed with recorded experiments at both ends of the composition range, a systematically greater separation occurred in the central portion where the variance was as much as 1.5 percent.

On the basis of the above considerations no further testing of the still was carried out.

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16. Gilmont and Othmer; op. cit., p. 1064 (Nov. 1944).

17. Fowler; op. cit., p. 828.

18. Struck and Kinney; op. cit., p. 79.

VAPOR PRESSURE OF METHYL BENZOATE

The still was cleaned out and dried and filled with 350 cc. of methyl benzoate to run a vapor pressure temperature curve. This was done primarily to check the operation of the still using a benzoate although the run also provided a check of the vapor pressure data available on methyl benzoate[19,20].

During the 50 mm. mercury pressure run with methyl benzoate the heating coils in the air bath were found to be inadequate to prevent fractionation because of the higher boiling range of the benzoates as compared to water. Therefore, the heating coils were shortened to cause more current to flow and consequently allow a higher air bath temperature to be attained. Also a floor was installed just above the liquid sample stopcock which eliminated about one cubic foot of excess space in the air bath.

The experimental temperatures and pressures obtained for methyl benzoate (Table IX) agreed quite well with those published in 1895-1898 (Figure 7). Assuming that the

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19. Kahlbaum, Georg W. A.; "Studien Uber Dampfspannkraftmessungen.II," Zeitschrift fur Physikalische Chemie, 26, 612 (1898).

20. Perry, John H.; Chemical Engineers Handbook, Revised third edition, McGraw-Hill Book Company, New York, 161 (1950).

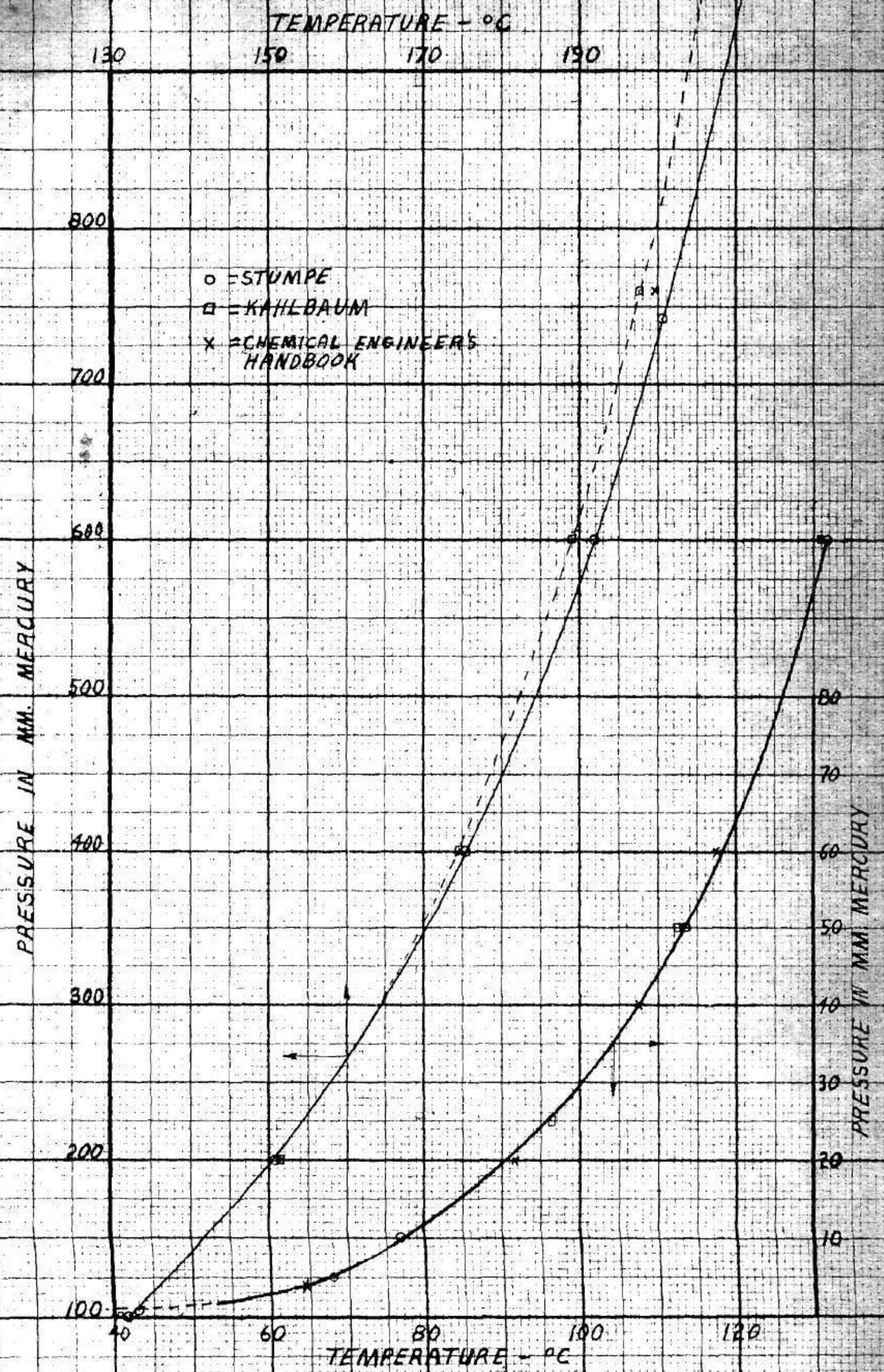

FIGURE 7
VAPOR PRESSURE CURVES FOR METHYL BENZOATE

literature values are correct, a check on the proper operation of the thermocouple and manometer is provided.

METHYL BENZOATE - ISOPROPYL BENZOATE SYSTEM

After the pure methyl benzoate run, new still solutions were prepared by withdrawing a predetermined volume of liquid and adding the proper quantity of isopropyl benzoate to make up the new solution. With any one solution equilibrium determinations were made at seven different pressures: 5, 10, 50, 100, 200, 400, and 760 mm. mercury absolute. All of the pressure runs for one solution were made in succession (Table X), rather than the alternative of all of the composition runs at any one pressure, in order to conserve expensive fluids.

The liquids would become yellowish due to decomposition of the isopropyl benzoate upon continued boiling* at 200 mm. mercury pressure or higher and contaminated with stopcock grease. Dow-Corning Corporation high vacuum silicones type grease was used and apparently did not react chemically and it precipitated out on cooling. Tests made before and after filtering out the grease with an asbestos mat proved that the grease did not appreciably affect the refractive index of the still liquids.

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* See page 4.

At the end of a series of pressure runs the yellowed, liquid was filtered to remove the colloidal grease suspension and distilled in a small unpacked column (Figure 8). The distillation was carried out at atmospheric pressure to avoid the bumping prevalent at reduced pressure. Heat was supplied to the 400 ml. boiling flask by a bunsen flame. A 28/15 ₸ ground glass joint connected the flask to a 10 inch lagged column ½ inch in diameter and wound with Number 20 nichrome wire to provide heat enough to prevent complete condensation before the vapors reached the condenser. The general design was similar to the Othmer still with the vapor sample and condensate return line replaced by a 500 ml. Erlenmeyer flask with a 24/40 ₸ ground glass joint. The water clear distillate was analyzed and made up to the proper composition and volume for the next run. By alternating two samples the distillation did not interfere with the equilibrium determinations.

The equilibrium samples were analyzed by comparison of the refractometer scale reading with a calibration chart (Figure 9) constructed from the refractometer scale reading versus the mole percent methyl benzoate of a standard set of samples (Table XI) which varied from zero to 100 mole percent methyl benzoate.

When all runs were complete the data was collected into the respective pressure groups and all of the data at

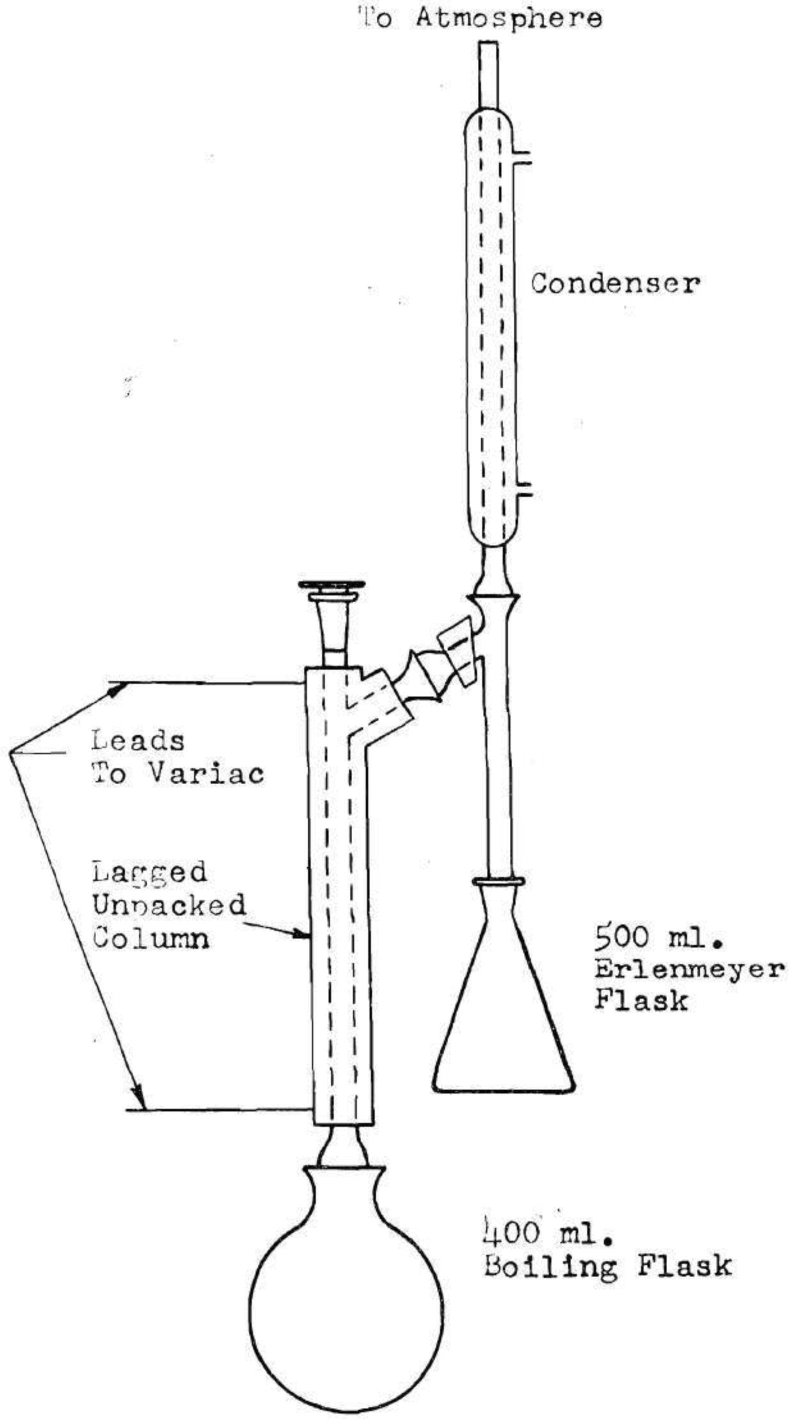

FIGURE 8
DISTILLATION EQUIPMENT

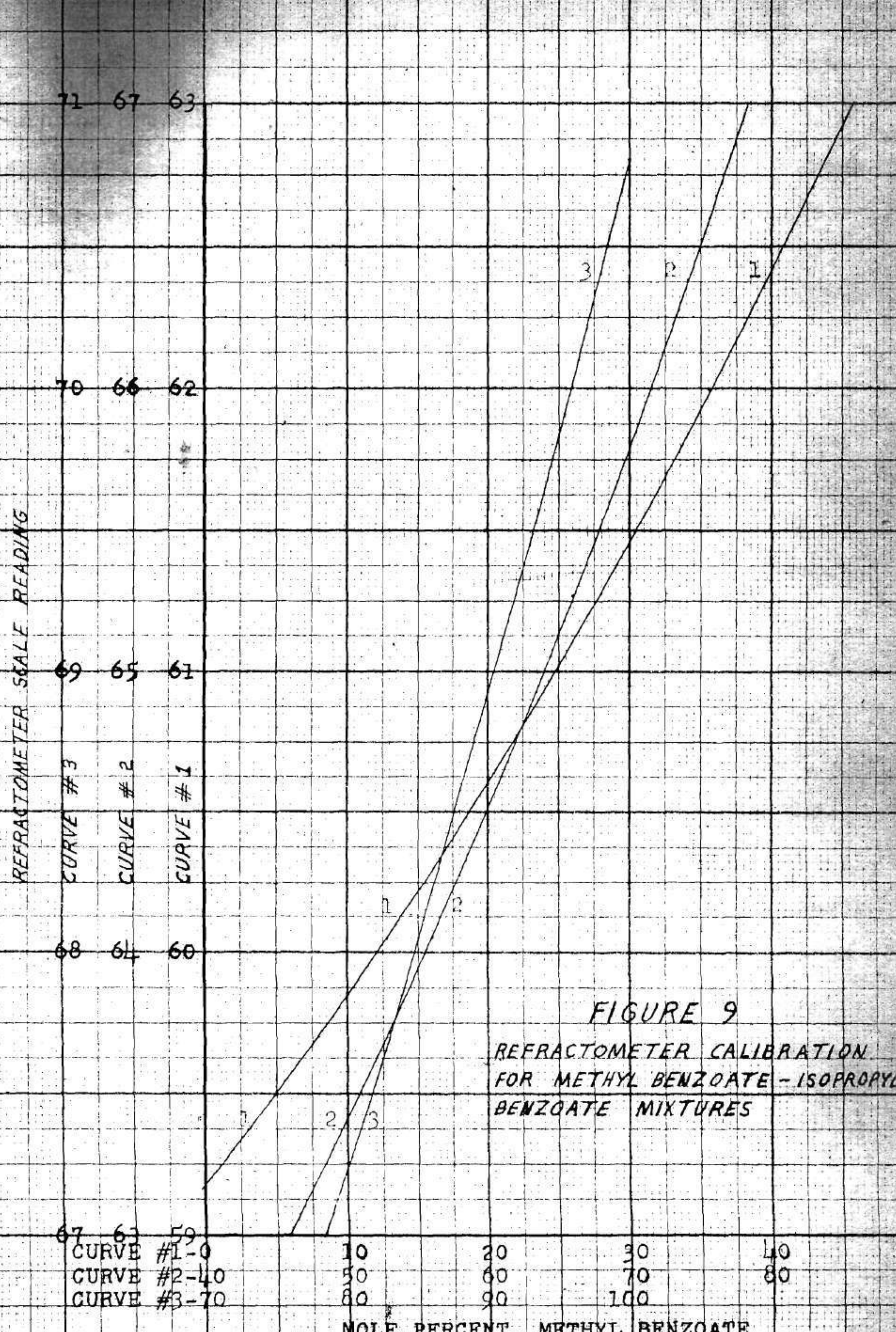

FIGURE 9
REFRACTOMETER CALIBRATION FOR METHYL BENZOATE - ISOPROPYL BENZOATE MIXTURES

any one pressure plotted on coordinate paper (graph not included) as mole precent methyl benzoate in the vapor versus mole percent methyl benzoate in the liquid. The resultant curves were fairly smooth and of the same general shape although some few points were apparently in error.

METHOD OF SMOOTHING DATA

The data were smoothed by the method of Othmer and Gilmont[21]. For this purpose the composition of the still liquid should be a constant. However, at the higher pressure runs, with a high isopropyl benzoate content, the apparent methyl benzoate concentration of the still liquid increased slightly. This was considered to be caused by a slight decomposition of the isopropyl benzoate which effected the refractive index. That it was not serious is shown by the fact that it did not appreciably affect the refractometer scale reading except at a high percent of isopropyl benzoate. Since the apparent increase in methyl benzoate concentration in the still liquid was less than one percent on the average,

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21. Othmer, Donald F. and Gilmont; "Correlating Vapor Compositions and related Properties of Solutions," Industrial and Engineering Chemistry, 36, 858 (Sept. 1944).

the equilibrium values of the still liquid observed during the 5, 10, and 50 mm. mercury pressure runs were assumed to be the correct values to use as the constant liquid compositions for purposes of smoothing the data.

Dalton's Law states that the mole fraction of a component of a gas is equal to its partial pressure fraction of the total pressure.

(1) $$y_1 = \frac{p_1}{P_T}$$

Taking the logarithm of both sides

(2) $$\log y_1 = \log p_1 - \log P_T$$

At a constant liquid composition this equation can be differentiated with respect to the logarithm of the total pressure

(3) $$\frac{d \log y_1}{d \log P_T} = \frac{d \log p_1}{d \log P_T} - \frac{d \log P_T}{d \log P_T}$$

(4) $$\frac{d \log Y_1}{d \log P_T} = \frac{d \log p_1}{d \log P_T} - 1$$

A rearrangement of the Claussius - Clapyeron equation[22] into

(5) $$\frac{d \log p_1}{d \log P_T} = \frac{L_1}{L_T}$$

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22. Perry; op. cit., p. 294.

And substitution into equation 4 gives

$$(6) \qquad d \log y_1 = \left[\frac{L_1}{L_T} - 1 \right] d \log P_T$$

Integration then gives

$$(7) \qquad \log y_1 = \left[\frac{L_1}{L_T} - 1 \right] \log P_T + C$$

When equation 7 is plotted on logrithmec coordinates the resulting lines should be straight (Figure 10). This method therefore permits points which are slightly in error to be corrected if Dalton's Law holds, and in general at pressures up to a few atmospheres this assumption[23] is as reliable as the experimental results.

Figure 10 was included to show that the experimental points fall more nearly on a straight line than on any other type of curve, but the actual smoothing of the data was done from a curve much larger than Figure 10, and too large to include in the thesis.

The smoothed points are listed in Table XII and the chart of the smoothed equilibrium curves is shown in Figure 11.

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23. Perry; op. cit., p. 291.

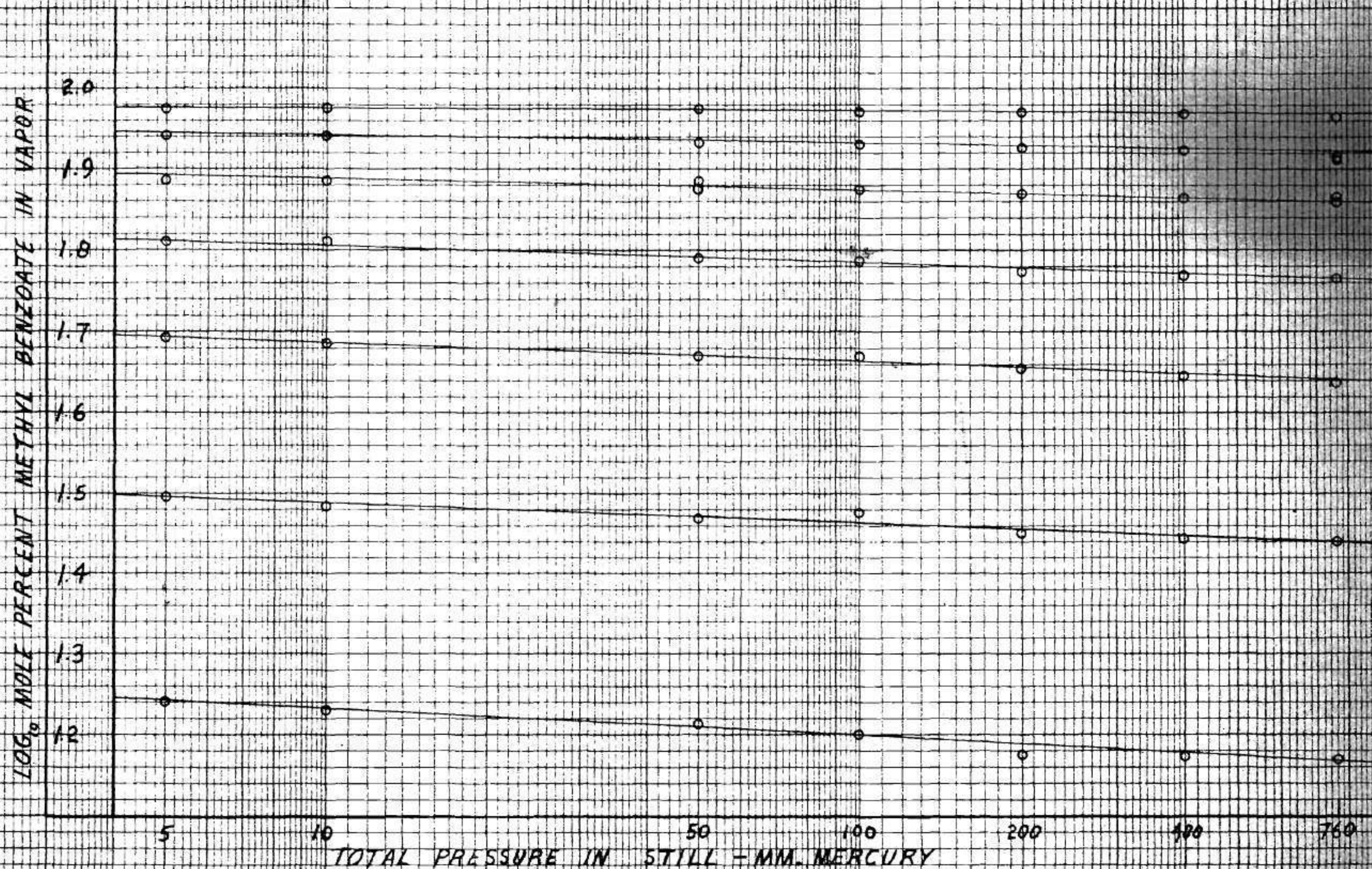

FIGURE 10: SMOOTHING OF DATA

COMPARISON WITH RAOULT'S LAW

To see how closely the benzoate system obeyed Raoult's Law, vapor pressure data for isopropyl benzoate were necessary.

A Duhring plot was used to determine the vapor pressure data of isopropyl benzoate because the supply of pure liquid became exhausted before this data could be obtained experimentally and time did not permit the ordering and purification of more.

In as much as the vapor pressure data obtained for methyl benzoate checked very closely with the recorded values and in as much as methyl benzoate and isopropyl benzoate are similar in structure, the method was believed to be as accurate as actual measurements would be over the whole range with isopropyl benzoate.

The vapor pressure of isopropyl benzoate at two different temperatures was available[24,25]. These data were sufficient to construct the Duhring chart (Figure 12) using methyl benzoate as the reference liquid. From this curve the vapor pressure curve for isopropyl benzoate was constructed (Figure 13).

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24. Table IV.

25. Matheson and Eastman Catalogs; (12 mm. at 94-96° C.).

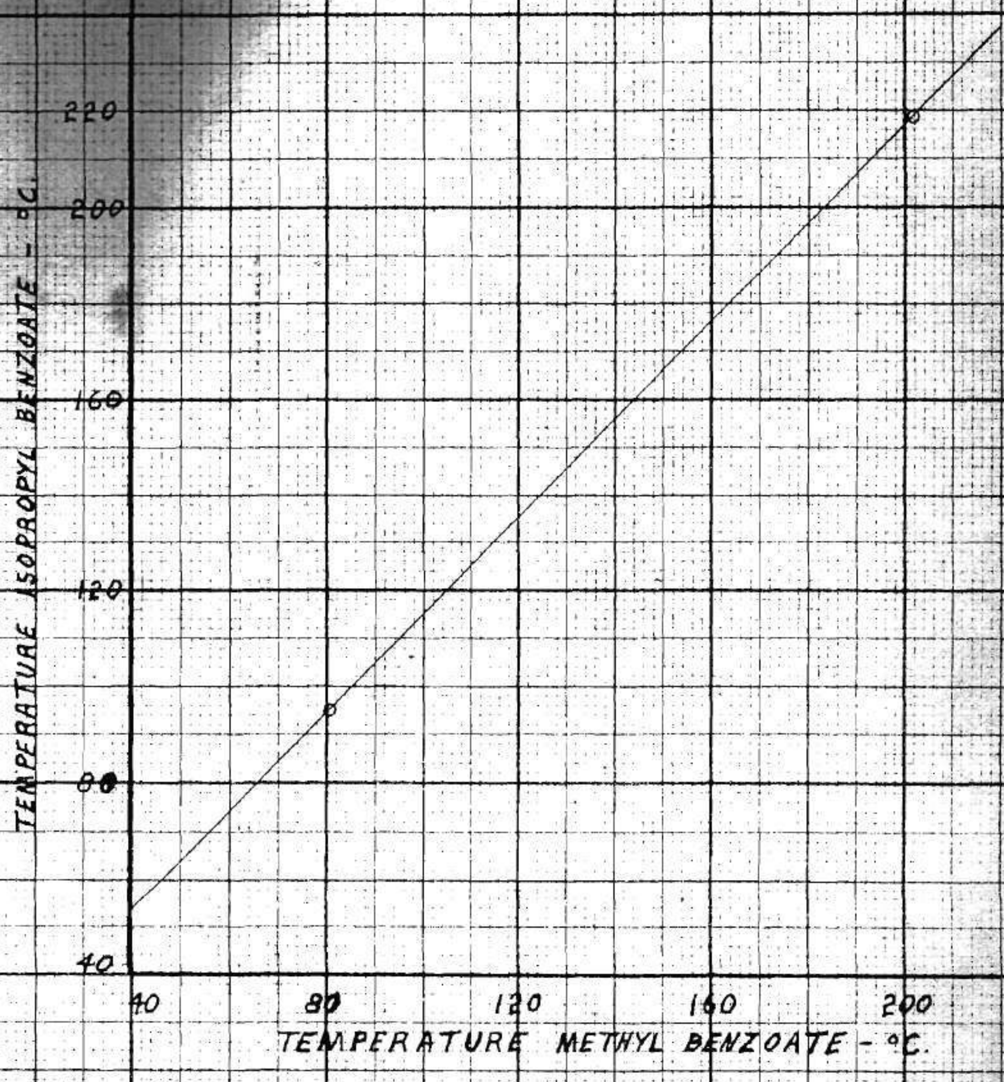

FIGURE 12
DÜHRING CHART FOR METHYL BENZOATE VS ISOPROPYL BENZOATE

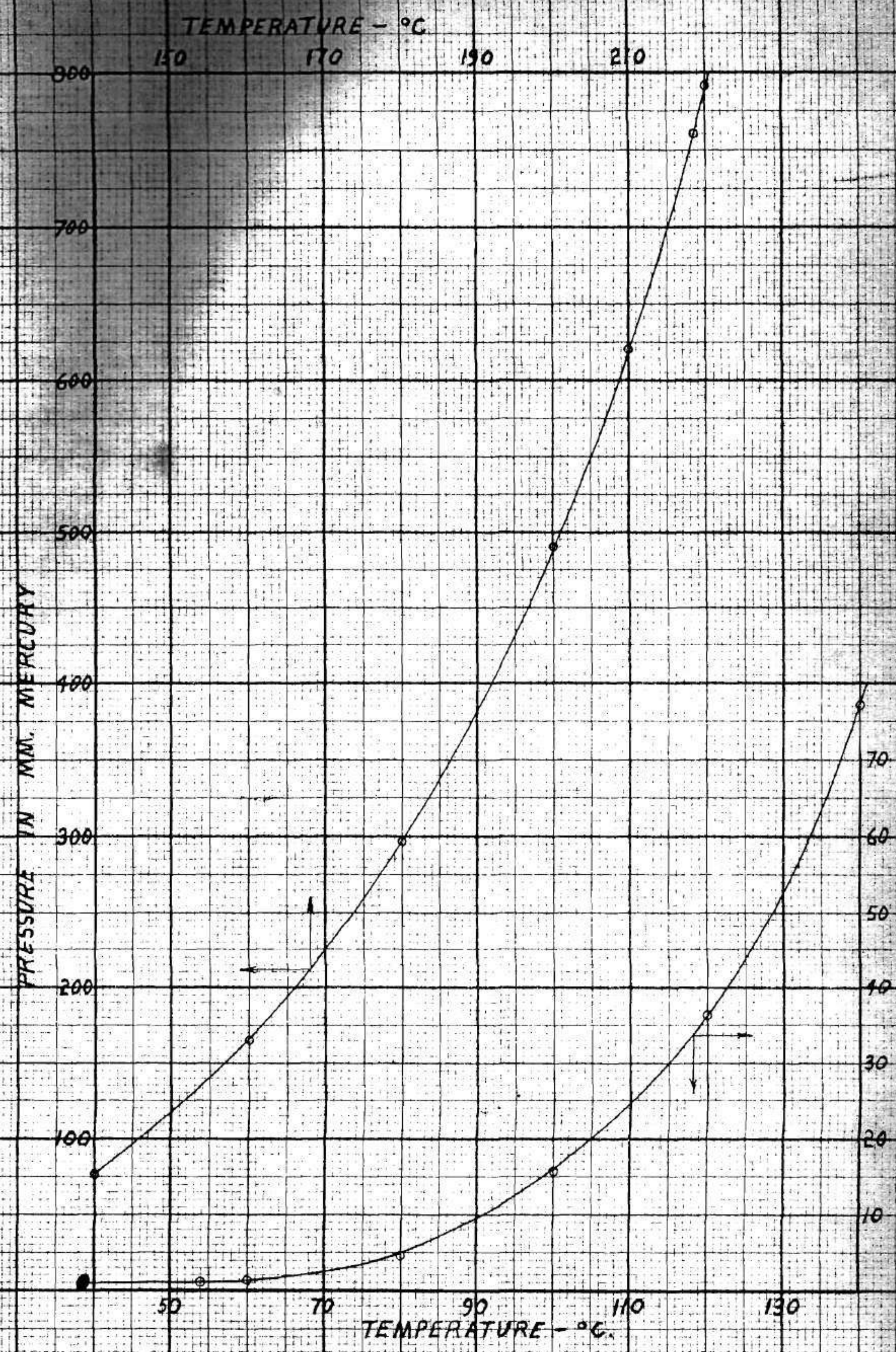

FIGURE 13
VAPOR PRESSURE CURVES FOR ISOPROPYL BENZOATE

Temperatures were arbitrabily selected and the corresponding vapor pressures for the pure liquids read off of the respective vapor pressure curves. Then using Raoult's Law,

$$p_1 = x_1 P_1^\circ \qquad p_2 = x_2 P_2^\circ$$

corresponding values of partial pressures of methyl benzoate and isopropyl benzoate and of total pressure were calculated for each of the seven liquid mixtures used experimentally. From these the equilibrium vapor and liquid compositions for each of the seven pressures investigated were easily calculated using Dalton's Law[26].

Table XIII lists the smoothed experimental values of vapor composition, the values by Raoult's Law, and the deviation. An examination of the deviations shows that this benzoate system obeys Raoult's Law at atmospheric pressure but apparently shows an increasing negative deviation as the pressure is reduced.

This result is contrary to theory and appears to be a combination of several probable factors which produced a cumulative effect on the value by Raoult's Law at low temperatures and pressures.

If the temperature of isopropyl benzoate at 12 mm. mercury pressure was lower by 6° Centigrade the shift in the

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26. See Page 35.

Duhring chart would change the Raoult's Law values so that they would agree almost exactly with the experimental values.

Another probable factor is in the construction of the methyl benzoate vapor pressure curve. The best curve drawn through points is a matter of individual judgment and, since the isopropyl benzoate curve was derived from the methyl benzoate curve, a slight variance of the methyl benzoate curve tends to throw the equilibrium values derived by Raoult's Law sharply toward or away from the experimental values.

The effect of a pressure variation is not very significant although a change of $\frac{1}{2}$ mm. mercury at a total pressure of 5 mm. could cause a slight change.

In consideration of these factors and, since it is highly improbable that a system would obey Raoult's Law at atmospheric pressure and not at lower pressures, it is believed that the system of methyl benzoate - isopropyl benzoate obeys Raoult's Law at all pressures and compositions.

CONCLUSIONS

The experimental Data for the system methyl benzoate - isopropyl benzoate are accurate to $\frac{1}{2}$ percent and have a maximum variation from Raoult's Law of one percent.

The apparent variation from Raoult's Law, amounting to 3.5 percent at 5 mm. mercury pressure, was probably caused by a combination of factors consisting of a wrong temperature value for isopropyl benzoate at 12 mm. mercury pressure, the construction of the vapor pressure curves, and perhaps a pressure variation.

An experimental determination of the isopropyl benzoate vapor pressure curve would provide Raoult's Law equilibrium values agreeing more nearly with the experimental values.

Raoult's Law may be safely used for calculations over the entire range of pressures and compositions.

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APPENDIX

TABLES

TABLE I

VAPOR PRESSURES OF METHYL BENZOATE BELOW ONE ATMOSPHERE[27]

Pressure mm. Mercury	Temperature °C.
1	43.0
10	77.3
25	96.3
50	112.6
100	130.8
200	151.4
400	174.7
600	188.9
760	197.5

27. Kahlbaum; op. cit., p. 612

TABLE II

VAPOR PRESSURES OF METHYL BENZOATE BELOW ONE ATMOSPHERE[28]

Pressure mm. Mercury	Temperature °C.
1	39.0
5	64.4
10	77.3
20	91.8
40	107.8
60	117.4
100	130.8
200	151.4
400	174.7
760	199.5

28. Perry; op. cit., p. 161.

TABLE III

DENSITY AND REFRACTIVE INDEX OF METHYL BENZOATE[29]

Temperature °C.	Density g/ml	Refractive Index n_d
30	1.0796	1.5074
35	1.0721	1.5032
40	1.0690	1.4987

REFRACTIVE INDEX FOR VARIOUS WAVE LENGTHS[30]

n	1.52049
n	1.51158
n	1.52890
n	1.53989

29. Phadke, S. R., et. al.; "Dipole Moments from Dielectric Constants of Liquids. Part I," Journal Indian Chemical Society, 22, 235 (1945).

30. Beilstein, 1st. Edition, IX-110 (1926).

TABLE IV

PHYSICAL CONSTANTS FOR METHYL BENZOATE AND ISOPROPYL BENZOATE[31]

	Methyl Benzoate	Isopropyl Benzoate
Molecular Weight g/mole	136.14	164.20
Color of Liquid	colorless	colorless
Index of Refraction	1.51810	———
Density g/ml	1.0937	1.0162
	1.088	———
Melting Point °C.	- 12.5	———
Boiling Point °C.	199.6	218.5

31. Hodgman, Charles, D.; Handbook of Chemistry and Physics, 30th Ed., Chemical Rubber Publishing Company, Cleveland, Ohio, 668 (1947).

TABLE V

COMMERCIAL DESCRIPTION OF ISOPROPYL BENZOATE[32]

"$C_6H_5COOCH(CH_3)_2$. Colorless liquid. M. W. 164.2; B. P., 218.5 °C. @ 760 mm.; sp. g., 1.016 @ 15/4 °C; Flash pt. (Cleveland Open Cup), 210 °F.; Substantially insol. in water; sol. in alcohol and organic solvents; odor, pleasantly aromatic. Chemical properties; undergoes ester exchange using customary catalysts to form other esters; rapidly reactive source of the benzoyl radical; undergoes the usual reactions of esters on reduction, or other treatment. Uses: Alkyd resin manfacture to control cross-linking, chemical intermediate for manufacture of other esters such as benzyl benzoate; high boiling solvent for inks, dyes, resins; odorant. Available in commercial quantities. Carbide and Carbon Chemicals Div."

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32. "New Chemicals for Industry," Chemical Industries, 67, 252 (Aug. 1950).

TABLE VI

UNSMOOTHED EQUILIBRIUM DATA FOR ACETIC ACID-WATER SYSTEM TAKEN FROM THE LITERATURE[33]

125 mm. MERCURY TOTAL PRESSURE

Weight Percent Water in Liquid	Weight Percent Water in Vapor
35.6	44.2
45.7	53.8
60.1	66.2
71.3	75.6

33. Gilmont and Othmer; op. cit., p. 1062 (Nov. 1944).

TABLE VII

REFRACTOMETER SCALE READING VERSUS COMPOSITION FOR THE ACETIC ACID-WATER SYSTEM AT 43° C.

Sample Number	Weight Percent Water	Refractometer Scale Reading
1	41.7	26.53
2	50.4	25.82
3	57.3	25.18
4	71.7	23.75

TABLE VIII

EXPERIMENTAL EQUILIBRIUM DATA FOR ACETIC ACID-WATER SYSTEM

Pressure	Weight % Water in Liquid	Weight Percent Water in Vapor
125	51.6	59.8
125	47.1	56.2
125	46.0	55.8
125	47.9	57.8
128	52.8	62.7
128	46.0	56.6
128	50.4	60.8

TABLE IX

EXPERIMENTAL VAPOR PRESSURE DATA FOR METHYL BENZOATE

Temperature of Vapor °C.	Pressure mm. Mercury
68.0	5
77.0	10
113.6	50
131.8	100
150.8	200
175.5	400
192.0	600
200.4	742

TABLE X

EXPERIMENTAL EQUILIBRIUM DATA FOR THE BENZOATES

A*	B*	C*	D*	E*	F*
Run 1, At 90.6 Mole Percent Methyl Benzoate					
68.0	5	69.04	90.6	69.78	94.7
79.3	10	69.04	90.6	69.78	94.7
115.1	50	69.10	91.0	69.75	94.5
135.8	100	69.04	90.6	69.52	93.3
157.0	200	69.04	90.6	69.50	93.2
181.1	400	69.04	90.6	69.45	92.9
208.5	760	69.04	90.6	69.30	92.1
Run 2, At 79.0 Mole Percent Methyl Benzoate					
65.0	5	67.10	79.0	68.38	86.9
79.7	10	67.10	79.0	68.38	86.9
115.8	50	67.10	79.0	68.18	85.7
136.5	100	67.10	79.0	68.04	85.0
159.1	200	67.10	79.0	67.93	84.3
183.8	400	67.15	79.4	67.80	83.5
210.0	760	67.10	79.0	67.60	82.4
210.0	760	67.08	78.9	67.55	82.0
Run 3, At 65.3 Mole Percent Methyl Benzoate					
72.0	5	65.17	65.3	66.74	76.5
80.0	10	65.17	65.3	66.70	76.3
120.9	50	65.17	65.3	66.70	76.3
140.2	100	65.17	65.3	66.50	75.0
162.0	200	65.17	65.3	66.38	74.1
188.7	400	65.17	65.3	66.22	73.0
213.8	760	65.17	65.3	66.27	73.4

*A Temperature of Vapor, °C.
B Total Pressure, mm. Mercury.
C Scale Reading for Liquid Sample.
D Mole Percent Methyl Benzoate in Liquid.
E Scale Reading for Vapor Sample.
F Mole Percent Methyl Benzoate in Vapor.

TABLE X, continued

A*	B*	C*	D*	E*	F*
Run 4, At 49.0 Mole Percent Methyl Benzoate					
73.0	5	63.37	49.5	65.06	64.5
83.5	10	63.30	48.9	65.04	64.3
122.5	50	63.30	48.9	64.71	61.7
141.8	100	63.45	50.3	64.65	61.2
163.0	200	63.38	49.7	64.45	59.5
189.5	400	63.38	49.7	64.35	58.6
216.7	760	63.38	49.7	64.30	58.2
Run 5, At 35.0 Mole Percent Methyl Benzoate					
71.1	5	61.94	35.2	63.35	49.3
84.4	10	61.89	34.7	63.25	48.4
124.0	50	61.93	35.1	63.10	46.8
143.5	100	62.04	36.2	63.09	46.7
165.0	200	62.00	35.7	62.96	45.3
189.8	400	62.01	35.8	62.83	44.1
217.3	760	62.02	35.9	62.77	43.4
Run 6, At 20.2 Mole Percent Methyl Benzoate					
73.4	5	60.62	20.2	61.57	31.2
87.3	10	60.58	20.0	61.50	30.4
125.6	50	60.62	20.2	61.32	28.4
145.8	100	60.76	21.8	61.46	30.0
165.6	200	60.73	21.6	61.30	28.2
191.1	400	60.72	21.4	61.26	27.7
220.5	760	60.75	21.75	61.24	27.5
Run 7, At 10.6 Mole Percent Methyl Benzoate					
76.4	5	59.91	10.8	60.39	17.4
87.3	10	59.89	10.6	60.37	17.0
128.2	50	59.89	10.6	60.32	16.3
149.6	100	59.88	10.5	60.28	15.8
171.1	200	59.88	10.5	60.215	15.0
196.2	400	59.88	10.5	60.21	14.85
223.1	760	59.94	11.3	60.19	14.7

TABLE XI

REFRACTOMETER CALIBRATION FOR METHYL BENZOATE - ISOPROPYL BENZOATE MIXTURES AT 43° CENTIGRADE

Sample Number	Mole Percent Methyl Benzoate	Refractometer Scale Reading
1	0.0	59.17
2	12.86	60.05
3	24.40	60.97
4	35.64	62.00
5	46.33	63.05
6	56.10	64.06
7	65.98	65.27
8	75.22	66.55
9	83.84	67.85
10	92.24	69.37
11	100.0	70.81

TABLE XII

SMOOTHED EQUILIBRIUM VALUES

Temperature °C.	Mole Percent Methyl Benzoate in Liquid	Mole Percent Methyl Benzoate in Vapor
At 5 mm. Mercury Absolute Pressure		
78.4	10.6	17.4
73.6	20.2	31.1
71.1	35.0	49.3
73.0	49.0	64.4
72.0	65.3	77.6
65.0	79.0	87.1
68.0	90.6	94.6
At 10 mm. Mercury Absolute Pressure		
87.3	10.6	17.0
86.0	20.2	30.6
84.4	35.0	48.4
83.5	49.0	63.5
80.0	65.3	76.9
79.7	79.0	86.6
79.3	90.6	94.3
At 50 mm. Mercury Absolute Pressure		
128.2	10.6	16.1
125.6	20.2	29.3
124.0	35.0	46.8
122.5	49.0	61.5
120.9	65.3	75.3
115.8	79.0	85.5
115.1	90.6	93.8
At 100 mm. Mercury Absolute Pressure		
149.6	10.6	15.7
145.8	20.2	28.8
143.5	35.0	46.0
141.8	49.0	60.7
140.2	65.3	74.6
136.5	79.0	85.0
135.8	90.6	93.4

TABLE XII, continued

Temperature °C.	Mole Percent Methyl Benzoate in Liquid	Mole Percent Methyl Benzoate in Vapor
At 200 mm. Mercury Absolute Pressure		
171.1	10.6	15.3
165.6	20.2	28.4
165.0	35.0	45.3
163.0	49.0	59.8
162.0	65.3	73.9
159.1	79.0	84.5
157.0	90.6	93.2
At 400 mm. Mercury Absolute Pressure		
196.2	10.6	15.0
191.1	20.2	27.9
189.8	35.0	44.6
189.5	49.0	59.0
188.7	65.3	73.2
183.8	79.0	84.1
181.1	90.6	93.0
At 760 mm. Mercury Absolute Pressure		
223.1	10.6	14.6
220.5	20.2	27.5
217.3	35.0	44.0
216.7	49.0	58.2
213.8	65.3	72.6
210.0	79.0	83.7
208.5	90.6	92.8

TABLE XIII

COMPARISON WITH RAOULT'S LAW

Mole Percent Methyl Benzoate in Liquid	Mole Percent Methyl Benzoate in Vapor by Raoult's Law	Deviation of Raoult's Law Value from Smoothed Experimental Value
At 5 mm. Mercury Absolute Pressure		
10.6	19.2	1.8
20.2	34.0	2.9
35.0	52.8	3.5
49.0	68.0	3.6
65.3	80.0	2.4
79.0	88.6	1.5
90.6	96.0	1.4
At 10 mm. Mercury absolute Pressure		
10.6	18.6	1.6
20.2	32.8	2.2
35.0	52.1	3.7
49.0	66.8	3.3
65.3	79.0	2.1
79.0	88.0	1.4
90.6	96.0	1.7
At 50 mm. Mercury Absolute Pressure		
10.6	17.2	1.1
20.2	30.6	1.3
35.0	49.0	2.2
49.0	64.0	2.5
65.3	76.7	1.4
79.0	86.0	0.5
90.6	94.8	1.0
At 100 mm. Mercury Absolute Pressure		
10.6	16.5	0.8
20.2	30.0	1.2
35.0	48.0	2.0
49.0	63.0	2.3
65.3	76.0	1.4
79.0	86.0	1.0
90.6	95.0	1.6

TABLE XIII, continued

Mole Percent Methyl Benzoate in Liquid	Mole Percent Methyl Benzoate in Vapor by Raoult's Law	Deviation of Raoult's Law Value from Smoothed Experimental Value
At 200 mm. Mercury Absolute Pressure		
10.6	16.0	0.7
20.2	29.0	0.6
35.0	46.5	1.2
49.0	62.0	2.2
65.3	75.0	1.1
79.0	86.0	1.5
90.6	95.0	1.8
At 400 mm. Mercury Absolute Pressure		
10.6	15.5	0.5
20.2	28.2	0.3
35.0	45.0	0.4
49.0	60.8	1.8
65.3	74.5	1.3
79.0	85.0	0.9
90.6	93.8	0.8
At 760 mm. Mercury Absolute Pressure		
10.6	14.9	0.3
20.2	27.2	-0.3
35.0	44.1	0.1
49.0	59.2	1.0
65.3	73.0	0.4
79.0	84.2	0.5
90.6	93.3	0.5